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(54) Title: DYE-TRANSFER INHIBITORY PREPARATION, AND DETERGENT COMPOSITION COMPRISING SUCH A PREPARATION

(57) Abstract

A dye-transfer inhibitory preparation comprises granules containing co-granulated peroxidase and accelerator, and a detergent composition (e.g. suitable for laundry washing) comprises such a preparation. When coated with a slow-release coating, such dye-inhibitory preparations are well-suited for use in media containing relatively oxidation-sensitive functional components, such as other types of enzymes.

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DYE-TRANSFER INHIBITORY PREPARATION, AND DETERGENT COMPOSITION COMPRISING SUCH A PREPARATION

FIELD OF THE INVENTION

The present invention relates to a dye-transfer inhibitory preparation comprising a peroxidase and an accelerator, and to a detergent composition comprising such a dye-transfer inhibitory preparation. The invention further relates to a method of laundry washing (i.e. washing of textile or fabric articles, such as articles of clothing and the like) so as to inhibit fabric-to-fabric transfer of dye (or other colourant) during washing.

BACKGROUND OF THE INVENTION

The concept of dye-transfer inhibition, i.e. inhibition of fabric-to-fabric transfer of dye during washing, is described in, e.g., WO 91/05839, which discloses that dye-transfer inhibition can be achieved with a preparation comprising a peroxidase and "another oxidisable substrate" (see page 10, lines 7-19, of WO 91/05839), the first oxidisable substrate being the dye in question. For the sake of brevity, "another oxidisable substrate" as referred to above will be referred to hereinafter in the present specification with claims as an "accelerator".

Dye-transfer inhibition is a very sensitive process, and a very desirable goal in this connection is bleaching of the washing liquor (i.e. removal of coloration by degradation of dye dissolved in the washing liquor) by enzymatic means without discoloration of dye which remains fixed to the laundry articles undergoing washing.

On an industrial scale, dry (solid-phase) enzyme preparations are often manufactured and commercialized in the form of granules (often denoted "granulate"), produced in large-scale granulation plants. In order to adequately exploit the capacity of the available granulation facilities, a manufacturer producing a range of different types of granulates (e.g. containing different enzymes, or

containing different amounts of a particular enzyme) will normally need to switch periodically from production of one type of granulate to another in a given granulation plant.

With respect to the manufacture of a solid-phase, enzyme-containing preparation which comprises not only the enzyme(s) in question, but also one or more other functional components [and which is intended for use either in its own right or as a component (additive) to be subsequently incorporated in a more complex composition (such as a detergent composition)], it will be a great advantage from the point of view of maximizing the operational efficiency and economy of the granulation plant - including minimizing the amount of manpower needed for its operation - if all of the constituents of the enzyme-containing preparation can be incorporated together (i.e. co-granulated) in one type of granulate, thereby obviating the need to granulate the enzyme and the other functional component(s) separately and to subsequently combine these granulates in the appropriate proportions.

SUMMARY OF THE INVENTION

In the light of the above, a first aspect of the present invention provides a dye-transfer inhibitory preparation comprising granules containing co-granulated peroxidase and accelerator. It is generally preferable (e.g. from the point of view of robustness during handling, and prevention of dust formation) that the granules are coated with an appropriate coating; suitable coating agents for this purpose include substances such as polyethylene glycols (e.g. PEG 4000).

It has been observed that the inclusion of a peroxidase system (i.e. a peroxidase together with hydrogen peroxide or a source thereof) in compositions such as detergent compositions for laundry washing, can be problematical when the composition in question further contains, for example, other enzymes, e.g. proteases, lipases, cutinases, amylases and/or cellulases, added for the purpose of aiding in the removal of various kinds of soil or stain from the substrate(s) to be washed or cleaned. Thus, the rather aggressive oxidizing effect of peroxidase systems can

result in the inactivation of other enzymes present before those enzymes have been able to perform their intended function to a satisfactory extent.

In order to be able to satisfactorily exploit the dye-transfer inhibitory effect of peroxidase systems for incorporation in washing/cleaning preparations for industrial or household use which contain relatively oxidation-sensitive constituents, there is thus a need to reduce or eliminate the above-described, unwanted side effect of the peroxidase system, i.e. to ensure that relatively oxidation-sensitive functional components, such as other enzymes, present in the washing/cleaning system are able to perform their intended soil- or stain-removing function to a satisfactory extent.

Accordingly, in a preferred aspect of the present invention a dye-transfer inhibitory preparation of the invention is in the form of a slow-release coated co-granulate comprising a peroxidase and an accelerator (*vide supra*). It appears that the use of such a dye-inhibitory preparation of the invention in washing/cleaning compositions of the types mentioned above, e.g. detergent compositions for laundry washing, can result in significant reduction or elimination of the above-described, unwanted, oxidative side-effects of peroxidase systems, notably with respect to inactivation of other enzymes present before they have exerted their intended effect.

It will be thus generally be preferable, particularly when the peroxidase/-accelerator co-granulate preparation of the invention is a slow-release coated co-granulate, that the preparation is one in which one or more peroxidases is/are the only enzymatic component(s).

The use of a preparation of the invention as an supplement to, e.g., a laundry detergent composition results (*vide infra*) in very satisfactory inhibition of fabric-to-fabric transfer of dye (or other colouring material, e.g. from coloured stains) during a laundry washing process.

Dye-inhibitory preparations of the invention are also very well suited for use in the rinsing or washing of fabrics or textiles after they have been dyed, and preparations

of the invention may be employed, e.g., in conjunction with, or as a component of, compositions for this purpose. The scope of the invention encompasses such compositions.

A further aspect of the present invention relates to the use of a dye-transfer inhibitory preparation according to the invention in the manufacture of a detergent formulation for laundry washing, and the invention thus provides a detergent composition containing a dye-transfer inhibitory preparation of the invention.

Also in this connection, the invention relates to a method of laundry washing, wherein articles of laundry are washed in an aqueous washing medium to which has been added a dye-inhibitory preparation (or detergent composition) according to the invention.

DETAILED DISCLOSURE OF THE INVENTION

Peroxidases

Peroxidase enzymes (EC 1.11.1) employed in the context of the invention may very suitably be, e.g., any peroxidase comprised by the enzyme classification EC 1.11.1.7; peroxidase fragments, exhibiting peroxidase activity, as well as synthetic or semisynthetic peroxidase derivatives [e.g. with porphyrin ring systems, or microperoxidases (see, e.g., US 4,077,768, EP 0 537 381, WO 91/05858 and WO 92/16634)] are also relevant in the context of the invention. Suitable peroxidases are known from microbial, plant and animal origins.

Preferably, the peroxidase employed in the method of the invention is producible by plants (e.g. horseradish or soy bean peroxidase) or microorganisms such as fungi or bacteria. Some preferred fungi include strains belonging to the subdivision Deuteromycotina, class Hyphomycetes, e.g. *Fusarium*, *Humicola*, *Tricoderma*, *Myrothecium*, *Verticillum*, *Arthromyces*, *Caldariomyces*, *Ulocladium*, *Embellisia*, *Cladosporium* or *Dreschlera*, in particular *Fusarium oxysporum* (DSM 2672), *Humicola insolens*, *Trichoderma resii*, *Myrothecium verrucana* (IFO 6113), *Verticillum*

alboatrum, *Verticillum dahlie*, *Arthromyces ramosus* (FERM P-7754), *Caldariomyces fumago*, *Ulocladium chartarum*, *Embellisia allio*r *Dreschlera halodes*.

Other preferred fungi include strains belonging to the subdivision Basidiomycotina, class Basidiomycetes, e.g. *Coprinus*, *Phanerochaete*, *Coriolus* or *Trametes*, in particular *Coprinus cinereus* f. *microsporus* (IFO 8371), *Coprinus macrorhizus*, *Phanerochaete chrysosporium* (e.g. NA-12) or *Trametes* (previously called *Polyporus*), e.g. *T. versicolor* (e.g. PR4 28-A).

Further preferred fungi include strains belonging to the subdivision Zygomycotina, class Mycoraceae, e.g. *Rhizopus* or *Mucor*, in particular *Mucor hiemalis*.

Some preferred bacteria include strains of the order Actinomycetales, e.g. *Streptomyces spheroides* (ATTC 23965), *Streptomyces thermoviolaceus* (IFO 12382) or *Streptoverticillum verticillium* ssp. *verticillium*

Other preferred bacteria include *Bacillus pumilus* (ATCC 12905), *Bacillus stearothermophilus*, *Rhodobactersphaeroides*, *Rhodomonas palustri*, *Streptococcus lactis*, *Pseudomonas purrocinia* (ATCC 15958) or *Pseudomonas fluorescens* (NRRL B-11).

Further preferred bacteria include strains belonging to *Myxococcus*, e.g. *M. virescens*.

Other relevant peroxidases are "haloperoxidases" (see, e.g., US 4,937,192), such as chloride peroxidases (EC 1.11.1.10), bromide peroxidases, and iodide peroxidases (EC 1.11.1.8).

Other potential sources of useful particular peroxidases are listed in B.C. Saunders et al., *Peroxidase*, London, 1964, pp. 41-43.

The peroxidase may furthermore be one which is producible by a method comprising cultivating a host cell transformed with a recombinant DNA vector which carries a DNA sequence encoding said peroxidase as well as DNA sequences encoding functions permitting the expression of the DNA sequence encoding the peroxidase, in a culture medium under conditions permitting the expression of the peroxidase and recovering the peroxidase from the culture.

Particularly, a recombinantly produced peroxidase is a peroxidase derived from a *Coprinus* sp., in particular *C. macrorhizus* or *C. cinereus* according to WO 92/16634.

As already indicated to some extent above, the term peroxidase as employed in the context of the invention embraces substances possessing peroxidase activity, such as peroxidase-active fragments derived from cytochromes, hemoglobin or peroxidase enzymes, and synthetic or semisynthetic derivatives thereof, e.g. iron porphins, iron porphyrins and iron phthalocyanine and derivatives thereof.

The peroxidase employed in a preparation of the invention will very suitably often be a *Coprinus* peroxidase, a *Myxococcus* peroxidase, or a horseradish peroxidase.

A preferred embodiment of a dye-transfer inhibitory preparation according to the invention contains peroxidase in an amount of from 0.01 to 100 mg enzyme protein/g of preparation, preferably 0.1-20 mg enzyme protein/g of preparation.

Accelerators

The accelerator can be any suitable peroxidase accelerator. Examples of accelerators include the following: halide ions (e.g. chloride and bromide); certain metal ions (e.g. Mn^{2+}); phenolic species (e.g. p-hydroxycinnamic acid, 2,4-dichlorophenol, vanillin, 7-hydroxycoumarin, 6-hydroxy-2-naphthoic acid, and p-hydroxybenzenesulfonate); 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate (ABTS; see, e.g., WO 94/12620); and 10-methyl-, 10-ethyl- and 10-propyl-phenothiazine (see, e.g., WO 94/12621). Numerous other accelerators are disclosed in WO 94/12619, WO 94/12620 and WO 94/12621.

Preferred accelerators in the context of the present invention are 10-phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621), and dye-transfer inhibitory co-granulate preparations of the invention comprising such accelerators have good storage stability (shelf life), and lead to very satisfactory dye-transfer inhibition in fabric washing (*vide infra*).

Accelerator is preferably present in a preparation of the invention in an amount of from 10^{-7} to 10^{-2} mol/g of preparation, preferably from 10^{-5} to 10^{-3} mol/g of preparation.

Coatings

The coating will normally be applied to the peroxidase- and accelerator-containing granulate (co-granulate) in an amount in the range of 5-50% by weight (calculated on the basis of the weight of the uncoated, dry granulate), preferably in the range of 10-40% by weight. The amount of coating to be applied to the granulate will depend to a considerable extent on the nature and composition of the desired coating.

Suitable slow-release coatings are coatings which give rise to slow release of the contents of the granules of a dye-transfer inhibitory preparation (co-granulate) of the invention under the conditions prevailing during the use thereof. Thus, for example, when a preparation of the invention is to be introduced into a washing liquor containing a washing detergent (normally comprising, e.g., one or more types of surfactant), the coating should be one which ensures slow release of peroxidase from the co-granulate when it is introduced into the washing medium.

Preferred slow-release coatings are coatings which are substantially insoluble in water.

Slow-release coatings which are appropriate in the context of dye-transfer inhibition in washing media may suitably comprise substances selected from the following: tallow; hydrogenated tallow; partially hydrolyzed tallow; fatty acids and fatty alcohols

of natural and synthetic origin; long-chain fatty acid mono-, di- and triesters of glycerol (e.g. glycerol monostearate); ethoxylated fatty alcohols; latexes; hydrocarbons of melting point in the range of 50-80°C; and waxes.

Melt-coating agents are a preferred class of slow-release coating agents which can be used without dilution with water.

Reference may be made to *Controlled Release Systems: Fabrication Technology, Vol. I*, CRC Press, 1988, for further information on slow-release coating.

Coatings in general, including slow-release coatings, may suitably further comprise substances such as clays (e.g. kaolin), titanium dioxide, pigments, salts (such as calcium carbonate) and the like. The person skilled in the art will be aware of further coating constituents of relevance in the present context.

Granules

The peroxidase- and accelerator-containing granules (i.e. disregarding any coating) of a preparation of the invention may suitably further contain various granulation aids, binders, fillers, lubricants and the like. Examples hereof include cellulose (e.g. cellulose in fibre or microcrystalline form), dextrins (e.g. yellow dextrin), polyvinylpyrrolidone, polyvinylalcohol, cellulose derivatives (such as CMC or hydroxypropylcellulose), gelatin, salts (e.g. sodium sulfate, sodium chloride, calcium sulfate or calcium carbonate), titanium dioxide, talc and clays (e.g. kaolin or bentonite).

Other materials of relevance for incorporation in the granules of the type in question are described, for example, in EP 0 304 331 B1, and will be well known to persons skilled in the art.

Methods and apparatus for producing enzyme-containing granulates are likewise well known to the skilled person (see, e.g., EP 0 304 331 B1). Compact granulates - produced, e.g., using apparatus comprising knives as described in Example 1 in

US Patent No. 4,106,991 - constitute very suitable granulates (co-granulates) in the context of the invention.

Detergent composition

As already mentioned, the present invention also relates to a detergent composition. Preferred embodiments of such a detergent composition will contain between 0.01 and 10% by weight (w/w) of the dye-transfer inhibitory preparation, preferably between 0.1 and 2% w/w thereof. A detergent composition according to the invention may be in any convenient form, e.g. in the form of powder, granules or paste containing a dye-inhibitory preparation of the invention.

A detergent composition of the invention will generally further comprise a source of hydrogen peroxide. Suitable sources thereof are well known, and include, e.g., perborates and percarbonates. Such sources of hydrogen peroxide are commonly incorporated into detergents (*vide infra*) as bleaching systems directed at oxidizable stains in the laundry.

A detergent composition according to the invention comprises one or more surfactants, each of which may be anionic, nonionic, cationic, or zwitterionic. It will usually contain 0-50% of anionic surfactant such as linear alkylbenzenesulfonate (LAS), alpha-olefinsulfonate (AOS), alkyl sulfate (fatty alcohol sulfate) (AS), alcohol ethoxysulfate (AEOS or AES), secondary alkanesulfonates (SAS), alpha-sulfo fatty acid methyl esters, alkyl- or alkenylsuccinic acid or soap. It may also contain 0-40% of nonionic surfactant such as alcohol ethoxylate (AEO or AE), carboxylated alcohol ethoxylates, nonylphenol ethoxylate, alkylpolyglycoside, alkyldimethylamineoxide, ethoxylated fatty acid monoethanolamide, fatty acid monoethanolamide, or polyhydroxy alkyl fatty acid amide (e.g. as described in WO 92/06154).

A detergent composition according to the invention may additionally comprise one or more other enzymes, such as an amylase, a lipase, a cutinase, a protease a cellulase or an oxidase (e.g. a laccase).

Enzymes (e.g. proteases) incorporated in the detergent composition according to the invention may be stabilized by means of conventional stabilizing agents, e.g. a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, a boric acid derivative such as, e.g., an aromatic borate ester, or an organoboronic or -borinic acid, and the detergent according to the invention may be formulated as described in, e.g., WO 92/19709 and WO 92/19708.

Where appropriate, enzymes may be incorporated in the detergent composition in the form of, e.g., a non-dusting granulate or a protected enzyme. Non-dusting granulates may be produced, e.g., as disclosed in US 4,106,991 and 4,661,452 (both to Novo Industri A/S) and may optionally be coated by methods known in the art. Examples of waxy coating materials are poly(ethylene oxide) products (polyethyleneglycol, PEG) with mean molecular weights of 1000 to 20000. Examples of film-forming coating materials suitable for application by fluid bed techniques are given in patent GB 1483591. Protected enzymes may be prepared according to the method disclosed in EP 238,216.

A detergent composition according to the invention may contain 1-65% of a detergent builder or complexing agent such as zeolite, diphosphate, triphosphate, phosphonate, citrate, nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTMPA), alkyl- or alkenylsuccinic acid, soluble silicates or layered silicates (e.g. SKS-6 from Hoechst). A detergent composition according to the invention may also be unbuilt, i.e. essentially free of detergent builder.

A detergent composition according to the invention may comprise one or more polymers. Examples are carboxymethylcellulose (CMC), poly(vinylpyrrolidone) (PVP), polyethyleneglycol (PEG), poly(vinyl alcohol) (PVA), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

As already indicated, a detergent composition according to the invention may contain a bleaching system which may comprise a H_2O_2 source such as perborate or percarbonate which may be combined with a peracid-forming bleach activator such as tetraacetylethylenediamine (TAED) or nonanoyloxybenzenesulfonate (NOBS). Alternatively, the bleaching system may comprise peroxyacids of, e.g., the amide, imide, or sulfone type.

A detergent composition according to the invention may also contain other conventional detergent ingredients such as e.g. fabric conditioners including clays, foam boosters, suds suppressors, anti-corrosion agents, soil-suspending agents, anti-soil redeposition agents, dyes, bactericides, optical brighteners, or perfume.

The pH (measured in aqueous solution at use concentration) will usually be neutral or alkaline, e.g. in the range of 7-11.

Particular forms of detergent composition according to the invention include:

1) A detergent composition formulated as a granulate having a bulk density of at least 600 g/l comprising

Linear alkylbenzenesulfonate (calculated as acid)	7 - 12%
Alcohol ethoxysulfate (e.g. C_{12-18} alcohol, 1-2 EO) or alkyl sulfate (e.g. C_{16-18})	1 - 4%
Alcohol ethoxylate (e.g. C_{14-15} alcohol, 7 EO)	5 - 9%
Sodium carbonate (as Na_2CO_3)	14 - 20%
Soluble silicate (as $Na_2O,2SiO_2$)	2 - 6%
Zeolite (as $NaA1SiO_4$)	15 - 22%
Sodium sulfate (as Na_2SO_4)	0 - 6%
Sodium citrate/citric acid (as $C_6H_5Na_3O_7/C_6H_8O_7$)	0 - 15%

Sodium perborate (as $NaBO_3.H_2O$)	11 - 18%
TAED	2 - 6%
Carboxymethylcellulose	0 - 2%
Polymers (e.g. maleic/acrylic acid copolymer, PVP, PEG)	0 - 3%
Enzymes (calculated as pure enzyme protein)	0.00001 - 2%
Minor ingredients (e.g. suds suppressors, perfume, optical brightener, photobleach)	0 - 5%

2) A detergent composition formulated as a granulate having a bulk density of at least 600 g/l comprising

Linear alkylbenzenesulfonate (calculated as acid)	6 - 11%
Alcohol ethoxysulfate (e.g. C_{12-18} alcohol, 1-2 EO or alkyl sulfate (e.g. C_{16-18})	1 - 3%
Alcohol ethoxylate (e.g. C_{14-15} alcohol, 7 EO)	5 - 9%
Sodium carbonate (as Na_2CO_3)	15 - 21%
Soluble silicate (as $Na_2O,2SiO_2$)	1 - 4%
Zeolite (as $NaA1SiO_4$)	24 - 34%
Sodium sulfate (as Na_2SO_4)	4 - 10%
Sodium citrate/citric acid (as $C_6H_5Na_3O_7/C_6H_8O_7$)	0 - 15%
Carboxymethylcellulose	0 - 2%
Polymers (e.g. maleic/acrylic acid copolymer, PVP, PEG)	1 - 6%
Enzymes (calculated as pure enzyme protein)	0.00001 - 2%
Minor ingredients (e.g. suds suppressors, perfume)	0 - 5%

3) A detergent composition formulated as a granulate having a bulk density of at least 600 g/l comprising

Linear alkylbenzenesulfonate (calculated as acid)	5 - 9%
Alcohol ethoxylate (e.g. C_{12-15} alcohol, 7 EO)	7 - 14%
Soap as fatty acid (e.g. C_{16-22} fatty acid)	1 - 3%
Sodium carbonate (as Na_2CO_3)	10 - 17%
Soluble silicate (as $Na_2O,2SiO_2$)	3 - 9%
Zeolite (as $NaA1SiO_4$)	23 - 33%
Sodium sulfate (as Na_2SO4)	0 - 4%
Sodium perborate (as $NaBO_3.H_2O$)	8 - 16%
TAED	2 - 8%
Phosphonate (e.g. EDTMPA)	0 - 1%
Carboxymethylcellulose	0 - 2%
Polymers (e.g. maleic/acrylic acid copolymer, PVP, PEG)	0 - 3%
Enzymes (calculated as pure enzyme protein)	0.00001 - 2%
Minor ingredients (e.g. suds suppressors, perfume, optical brightener)	0 - 5%

4) A detergent composition formulated as a granulate having a bulk density of at least 600 g/l comprising

Linear alkylbenzenesulfonate (calculated as acid)	8 - 12%
Alcohol ethoxylate (e.g. C_{12-15} alcohol, 7 EO)	10 - 25%
Sodium carbonate (as Na_2CO_3)	14 - 22%
Soluble silicate (as $Na_2O,2SiO_2$)	1 - 5%
Zeolite (as $NaA1SiO_4$)	25 - 35%
Sodium sulfate (as Na_2SO_4)	0 - 10%
Carboxymethylcellulose	0 - 2%
Polymers (e.g. maleic/acrylic acid copolymer, PVP, PEG)	1 - 3%
Enzymes (calculated as pure enzyme protein)	0.00001 - 2%
Minor ingredients (e.g. suds suppressors, perfume)	0 - 5%

5) A detergent composition formulated as a granulate having a bulk density of at least 600 g/l comprising

Fatty alcohol sulfate	5 - 10%
Ethoxylated fatty acid monoethanolamide	3 - 9%
Soap as fatty acid	0 - 3%
Sodium carbonate (as Na_2CO_3)	5 - 10%
Soluble silicate (as $Na_2O,2SiO_2$)	1 - 4%
Zeolite (as $NaA1SiO_4$)	20 - 40%
Sodium sulfate (as Na_2SO_4)	2 - 8%
Sodium perborate (as $NaBO_3.H_2O$)	12 - 18%
TAED	2 - 7%
Polymers (e.g. maleic/acrylic acid copolymer, PEG)	1 - 5%
Enzymes (calculated as pure enzyme protein)	0.00001 - 2%
Minor ingredients (e.g. optical brightener, suds suppressors, perfume)	0 - 5%

6) A detergent composition formulated as a granulate comprising

Linear alkylbenzenesulfonate (calculated as acid)	8 - 14%
Ethoxylated fatty acid monoethanolamide	5 - 11%
Soap as fatty acid	0 - 3%
Sodium carbonate (as Na_2CO_3)	4 - 10%
Soluble silicate (as $Na_2O,2SiO_2$)	1 - 4%
Zeolite (as $NaA1SiO_4$)	30 - 50%
Sodium sulfate (as Na_2SO_4)	3 - 11%
Sodium citrate (as $C_6H_5Na_3O_7$)	5 - 12%
Polymers (e.g. PVP, maleic/acrylic acid copolymer, PEG)	1 - 5%
Enzymes (calculated as pure enzyme protein)	0.00001 - 2%
Minor ingredients (e.g. suds suppressors, perfume)	0 - 5%

7) A detergent composition formulated as a granulate comprising

Linear alkylbenzenesulfonate (calculated as acid)	6 - 12%
Nonionic surfactant	1 - 4%
Soap as fatty acid	2 - 6%
Sodium carbonate (as Na_2CO_3)	14 - 22%
Zeolite (as $NaA1SiO_4$)	18 - 32%
Sodium sulfate (as Na_2SO_4)	5 - 20%
Sodium citrate (as $C_6H_5Na_3O_7$)	3 - 8%
Sodium perborate (as $NaBO_3.H_2O$)	4 - 9%
Bleach activator (e.g. NOBS or TAED)	1 - 5%
Carboxymethylcellulose	0 - 2%
Polymers (e.g. polycarboxylate or PEG)	1 - 5%
Enzymes (calculated as pure enzyme protein)	0.00001 - 2%

Minor ingredients (e.g. optical brightener, perfume)	0 - 5%

8) A detergent composition formulated as a granulate having a bulk density of at least 600 g/l comprising

Anionic surfactant (linear alkylbenzene-sulfonate, alkyl sulfate, alpha-olefinsulfonate, alpha-sulfo fatty acid methyl esters, alkanesulfonates, soap)	25 - 40%
Nonionic surfactant (e.g. alcohol ethoxylate)	1 - 10%
Sodium carbonate (as Na_2CO_3)	8 - 25%
Soluble silicates (as Na_2O, $2SiO_2$)	5 - 15%
Sodium sulfate (as Na_2SO_4)	0 - 5%
Zeolite (as $NaA1SiO_4$)	15 - 28%
Sodium perborate (as $NaBO_3.4H_2O$)	0 - 20%
Bleach activator (TAED or NOBS)	0 - 5%
Enzymes (calculated as pure enzyme protein)	0.00001 - 2%
Minor ingredients (e.g. perfume, optical brighteners)	0 - 3%

9) Detergent formulations as described in 1) - 8) wherein all or part of the linear alkylbenzenesulfonate is replaced by (C_{12}-C_{18}) alkyl sulfate.

10) A detergent composition formulated as a granulate having a bulk density of at least 600 g/l comprising

(C_{12}-C_{18}) alkyl sulfate	9 - 15%
Alcohol ethoxylate	3 - 6%
Polyhydroxy alkyl fatty acid amide	1 - 5%
Zeolite (as $NaA1SiO_4$)	10 - 20%

Layered disilicate (e.g. SK56 from Hoechst)	10 - 20%
Sodium carbonate (as Na_2CO_3)	3 - 12%
Soluble silicate (as $Na_2O,2SiO_2$)	0 - 6%
Sodium citrate	4 - 8%
Sodium percarbonate	13 - 22%
TAED	3 - 8%
Polymers (e.g. polycarboxylates and PVP=	0 - 5%
Enzymes (calculated as pure enzyme protein)	0.00001 - 2%
Minor ingredients (e.g. optical brightener, photo bleach, perfume, suds suppressors)	0 - 5%

11) A detergent composition formulated as a granulate having a bulk density of at least 600 g/l comprising

(C_{12}-C_{18}) alkyl sulfate	4 - 8%
Alcohol ethoxylate	11 - 15%
Soap	1 - 4%
Zeolite MAP or zeolite A	35 - 45%
Sodium carbonate (as Na_2CO_3)	2 - 8%
Soluble silicate (as $Na_2O,2SiO_2$)	0 - 4%
Sodium percarbonate	13 - 22%
TAED	1 - 8%
Carboxymethyl cellulose	0 - 3%
Polymers (e.g. polycarboxylates and PVP)	0 - 3%
Enzymes (calculated as pure enzyme protein)	0.00001 - 2%
Minor ingredients (e.g. optical brightener, phosphonate, perfume)	0 - 3%

12) Detergent formulations as described in 1) - 11) which contain a stabilized or encapsulated peracid, either as an additional component or as a substitute for already specified bleach systems.

13) Detergent compositions as described in 1), 3), 5), 7) and 8) wherein perborate is replaced by percarbonate.

14) Detergent compositions as described in 1), 3), 5), 7), 8), 10) and 11) which additionally contain a manganese catalyst. The manganese catalyst may, e.g., be one of the compounds described in "Efficient manganese catalysts for low-temperature bleaching", Nature 369, 1994, pp. 637-639.

It is at present contemplated that a preparation of the invention will typically be incorporated in the detergent composition of the invention in an amount corresponding to 0.001-2 mg (calculated as pure enzyme protein) of peroxidase per liter of wash liquor.

The invention will be illustrated by the following examples:

EXAMPLE 1. Preparation of a dye-transfer inhibitory preparation of the invention (coated co-granulate containing peroxidase and accelerator)

Granulation

5.2 kg of cellulose fibres (Arbocel™ BC 200), 4.2 kg of accelerator (PPT), 2.4 kg of kaolin, 1.2 kg of yellow dextrin (TACKIDEX™ G 155)and 23.1 kg of sodium sulfate (all dry components) were mixed in a Lödige mixer FM-D 130.

The above mixed dry components were sprayed, with continuous mixing, with 2.3 kg of liquid peroxidase concentrate (56.7 mg enzyme protein/g; *Coprinus* peroxidase produced as described in Example 1 in EP 505 311) in which had been dissolved 3.6 kg of sucrose.

During and after spraying, a compact granulate was formed by means of the knives described in Example 1 in US Patent No. 4,106,991.

When the granulation was finished, the granulate was dried on a fluidized bed. The dry granulate was sieved, and the product fraction of size between 300 and 1000 μm was separated for coating.

Coating.

The granulate was heated to 60°C in a Lödige FM 50 mixer, and 3% of melted hydrogenated tallow (also heated to 60°C) was added under continuous mixing. When the tallow was distributed, the granulate was powdered with 3.5% of kaolin and 3.5% of titanium dioxide under continuous mixing. 3% of glycerol monostearate (heated to 60°C) was then added under continuous mixing. When the glycerol monostearate was distributed, the granulate was powdered with 1.5% of kaolin with mixing.

All percentages are weight percentages relative to the dry uncoated granulate.

After cooling, the coated co-granulate was sieved and the fraction in the size range 300-1100 μm was collected for use as a dye-transfer inhibitor preparation.

Fig. 1 shows a comparison of the dye-inhibitory effect of the following two additives in an aqueous washing liquor containing a commercial, European laundry washing detergent (Ariel™ Futur - a bleach-containing compact powder):

(i) A preparation (coated peroxidase/accelerator co-granulate) prepared as described in Example 1 (--*---*--).

(ii) liquid peroxidase concentrate added to the washing liquor together with predissolved PPT to give the same nominal final concentration of PPT at each peroxidase level as with the co-granulate preparation) (--□---□--).

The washing conditions were as follows:

Equipment: Terg-o-meter
Water hardness: 17°dH (demineralized water with $CaCl_2$ an $MgCl_2$ added in ratio 5:1)
Detergent concentration: 4g/l
Washing temperature: 35°C
Washing time: 15 minutes

The dye-bleeding fabric was cotton dyed with Chicago Sky Blue 6B, and the extent of dye transfer to white cotton tracer fabric was determined by measuring the Hunter color difference, ΔE, between tracer swatches washed together with dye-bleeding swatches at various levels of peroxidase as described above, and tracer swatches washed in the same washing medium but in the absence of dye-bleeding fabric.

It is apparent from Fig. 1 that the dye-transfer inhibitory effect of the coated peroxidase/PPT co-granulate preparation according to the invention is comparable to that of the additive based on liquid peroxidase concentrate.

Fig. 2 illustrates the close correspondence between the results (Hunter ΔE measurements) obtained in two sets of dye-transfer inhibition experiments with the peroxidase/PPT co-granulate preparation according to the invention. The conditions were in both cases as described above in connection with Fig. 1.

CLAIMS

1. A dye-transfer inhibitory preparation comprising granules containing co-granulated peroxidase and accelerator.

2. A preparation according to claim 1, wherein said granules are coated with a slow-release coating.

3. A preparation according to claim 1 or 2, wherein peroxidase is the only enzymatic component.

4. A preparation according to claim 2 or 3, wherein said slow-release coating is substantially water-insoluble.

5. A preparation according to claim 4, wherein said slow-release coating comprises a coating agent selected from the group consisting of: tallow; hydrogenated tallow; partially hydrolyzed tallow; glycerol monostearate; fatty acids and fatty alcohols of natural and synthetic origin; ethoxylated fatty alcohols; hydrocarbons of melting point in the range of 50-80°C; and waxes.

6. A preparation according to any one of claims 1-5, comprising a peroxidase obtainable from a *Coprinus* or *Myxococcus* species, or a horseradish peroxidase.

7. A preparation according to any one of the preceding claims, wherein peroxidase is present in an amount in the range of 0.01 to 100 mg enzyme protein/g of preparation, preferably 0.1 to 20 mg enzyme protein/g of preparation, and accelerator is present in an amount in the range of 10^{-7} to 10^{-2} mol/g of preparation, preferably 10^{-5} to 10^{-3} mol/g of preparation.

8. A preparation according to any one of the preceding claims, wherein said accelerator is selected from the group consisting of: 10-phenothiazinepropionic acid (PPT); 10-ethylphenothiazine-4-carboxylic acid (EPC); 10-methylphenoxazine; and 10-phenoxazinepropionic acid (POP).

9. A detergent composition comprising a preparation according to any one of claims 1-7.

10. A detergent composition according to claim 9, containing between 0.01 and 10% w/w, preferably between 0.1 and 2% w/w, of a preparation according to any one of claims 1-7.

11. A method of laundry washing, wherein articles of laundry are washed in an aqueous washing medium containing a preparation according to any one of claims 1-8 or a detergent composition according to claim 9 or 10.

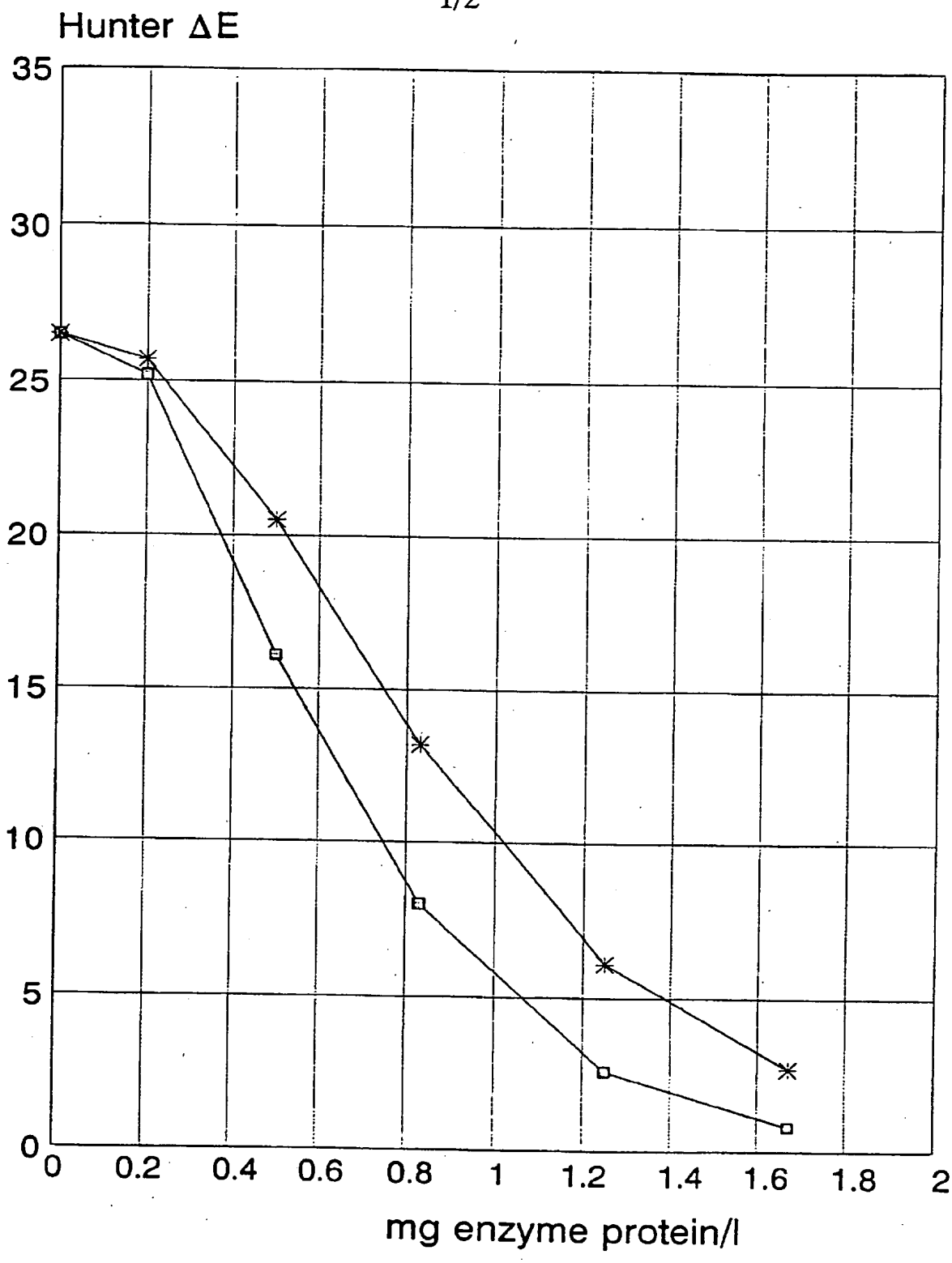
Hunter ΔE
35
30
25
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
mg enzyme protein/l

FIG. 1

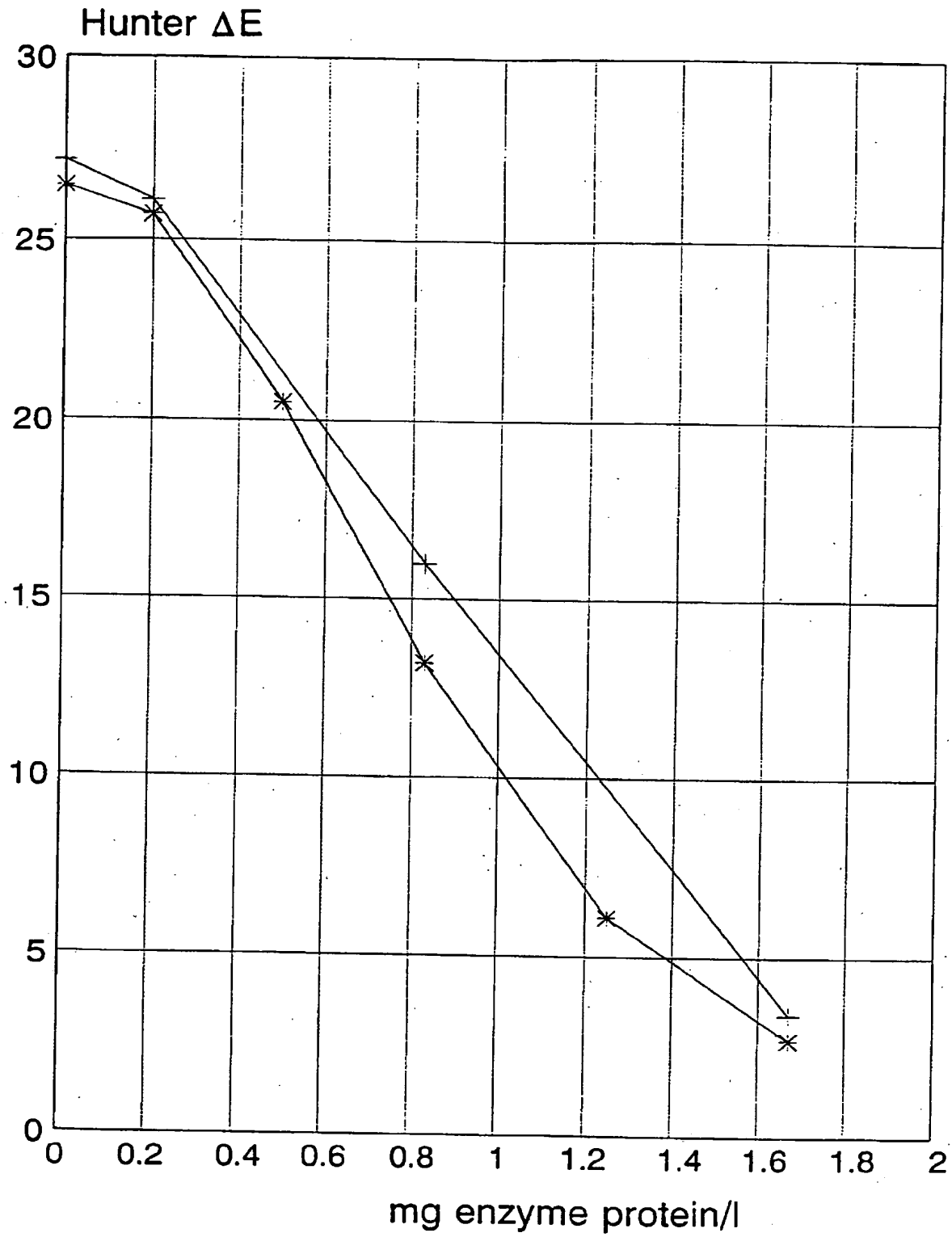
Hunter ΔE
30
25
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
mg enzyme protein/l

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/DK 95/00214

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C11D 3/386, C12N 9/98
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C11D, C12N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 9105839 A1 (NOVO NORDISK A/S), 2 May 1991 (02.05.91), page 3, line 6 - line 10; page 3, line 7 - line 25, claims 26,28,31 --	1-11
Y	WO 9015856 A1 (NOVO NORDISK A/S), 27 December 1990 (27.12.90), page 3, line 19 - line 20; page 5, line 11 - line 13, claims 1,2,4,5 --	1-11
P,A	WO 9412621 A1 (NOVO NORDISK), 9 June 1994 (09.06.94) -- --------	1-11

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"B" erlier document but published on or after the international filing date
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"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 Sept 1995	21.09.1995
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Dagmar Järvman Telephone No. +46 8 782 25 00

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

28/08/95

International application No.
PCT/DK 95/00214

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